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(54) Title: MULTIMODAL POLYETHYLENE MATERIAL

(57) Abstract: The present invention relates to a polyethylene resin having a multimodal molecular weight distribution, said resin being further characterized in that it has a density in the range of from about 0.925 g/ccm to about 0.950 g/ccm, a melt index (I₂) in the range of from about 0.05 g/10 min to about 5 g/10 min, and in that it comprises at least one high molecular weight (HMW) ethylene interpolymer and at least a low molecular weight (LMW) ethylene polymer, and a composition comprising such resin. Also provided is a shaped article comprising said resin or composition, in particular a pipe.



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MULTIMODAL POLYETHYLENE MATERIAL

5 The present invention relates to a multimodal polyethylene resin, a composition comprising such resin and to applications of such resin or composition, for example to make a shaped article. The resin and composition of the invention are particularly suitable for use in pipes.

10 Polyethylene compositions with a multimodal molecular weight distribution (MWD), for example a bimodal MWD, can offer distinct advantages compared with unimodal polyethylenes or other polyolefins. For example, bimodal polyethylenes may combine the favorable mechanical properties afforded by a high molecular weight polyethylene with the good processability of a low molecular weight polyethylene. The prior art reports that such materials can advantageously be employed in various applications, including film or pipe applications. Prior art multimodal polyethylenes suggested for use in pipes include the materials disclosed in the PCT applications with the
15 publication numbers WO 97 /29152, WO 00/ 01765, WO 00/18814, WO 01/02480 and WO 01/25328.

In view of the potentially disastrous consequences of material failures, acceptance of any plastic pipe for water or gas distribution is subject to product standards and performance requirements set forth in norms, for example, DIN (German Industrial Norm
20 or "Deutsche Industrie Norm") or norms defined by ISO (International Organization for Standardization, Geneva, Switzerland). For example, state of the art polyethylene materials sold into pipe applications, such as pressure pipes or irrigation pipes, meet the so-called PE80 or PE100 ratings (PE stands for polyethylene). Pipes manufactured from polyethylenes classifying as PE80-type or PE100-type resins must withstand a minimum
25 circumferential stress, or hoop stress, of 8 MPa (PE80) or 10 MPa (PE100) at 20°C for 50 years. PE100 resins are high density polyethylene (HDPE) grades typically having a density of at least about 0.950 g/ccm³ or higher.

Their relatively poor Long Term Hydrostatic Strength (LTHS) at high temperatures has been an acknowledged disadvantage of traditional polyethylenes which rendered these
30 materials unsuitable for use in piping with exposure to higher temperatures, such as domestic pipe applications. Domestic pipe systems typically operate at pressures between about 2 and about 10 bar and temperatures of up to about 70°C with malfunction

temperatures of about 95 - 100°C. Domestic pipes include pipes for hot and/or cold water in pressurized heating and drinking water networks within buildings as well as pipes for snow melt or heat recovery systems. The performance requirements for the various classes of hot water pipes, including underfloor heating, radiator connectors and sanitary pipes are
5 specified, for example, in International Standard ISO 10508 (first edition October 15, 1995, "Thermoplastic pipes and fittings for hot and cold water systems").

Materials which are typically used for piping with exposure to higher temperatures include polybutylene, random copolymer polypropylene and cross-linked polyethylene (PEX). The crosslinking of the polyethylene is needed to obtain the desired LTHS at high
10 temperatures. The crosslinking can be performed during extrusion, resulting in lower output, or in a post extrusion process. In both cases crosslinking generates significantly higher costs than thermoplastic pipe extrusion.

Polyethylenes of Raised Temperature Resistance (PE-RT), as defined in ISO-1043-1, are a class of polyethylene materials for high temperature applications which has recently
15 been introduced to the pipe market. Present PE-RT resins compare unfavorably with PEX materials in some respects, for example, in that the walls of PE-RT based pipes need to be thicker than those of PEX-based pipes due to lower stress ratings.

There still is the need for new polyethylene materials which offer an advantageously balanced combination of thermal, mechanical and processing properties. In particular, there
20 still is the need for new polyethylene materials, which afford superior high temperature resistance (e.g., in the range of operating temperatures from about 40°C to about 80°C and test temperatures of up to about 110°C), high stress resistance, good tensile and impact performance and excellent processability without having to be crosslinked. It is an object of the present invention to meet these and other needs.

25 The present invention provides a polyethylene resin with a multimodal molecular weight distribution. Said multimodal polyethylene resin is characterized in that it has a density in the range of from about 0.925 g/ccm to about 0.950 g/ccm and a melt index in the range of from about 0.05 g/10 min to about 5 g/10 min.

The present invention also provides a composition comprising such multimodal
30 polyethylene resin and at least one other component.

Other aspects of the invention relate to applications of such multimodal polyethylene resin and composition and to shaped articles made from such polyethylene resin or

composition. One particular embodiment of the present invention relates to durable applications, such as pipes.

The term “comprising” as used herein means “including”.

5 The term “interpolymer” is used herein to indicate polymers prepared by the polymerization of at least two monomers. The generic term interpolymer thus embraces the terms copolymer, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different monomers, such as terpolymers.

10 Unless indicated to the contrary, all parts, percentages and ratios are by weight. The expression “up to” when used to specify a numerical range includes any value less than or equal to the numerical value which follows this expression. The expression “from to” when used to specify a numerical range includes any value equal to or higher than the numerical value which follows this expression. In these contexts, the word “about” is used to indicate that the specified numerical limit represents an approximate value which may vary by 1 %, 15 2%, 5% or sometimes 10%.

“HMW” stands for high molecular weight, “LMW” stands for low molecular weight.

The abbreviation “ccm” stands for cubic centimeters.

20 Unless expressly specified otherwise, the term “melt index” means the I_2 melt index, as determined in accordance with ASTM D1238 under a load of 2.16 kg and at a temperature of 190°C.

Unless specified otherwise, the term “alpha-olefin” (α -olefin) refers to an aliphatic or cyclo-aliphatic alpha-olefin having at least 4, preferably from 4 to 20 carbon atoms.

25 The present invention provides a polyethylene resin having a multimodal molecular weight distribution, said resin being further characterized in that it has

(a) a density in the range of from about 0.925 g/ccm, preferably of from about 0.935 g/ccm, to about 0.950 g/ccm, preferably to about 0.945 g/ccm, and

(b) a melt index (I_2) in the range of from about 0.05 g/10 min, preferably of from about 0.1 g/10 min, to about 5 g/10 min, preferably to about 1 g/10 min.

30 Said multimodal polyethylene resin comprises at least one high molecular weight (HMW) ethylene interpolymer and at least a low molecular weight (LMW) ethylene polymer. The HMW interpolymer has a significantly higher weight average molecular

weight than the LMW polymer. Said difference in molecular weight is reflected in distinct melt indices. Preferred is a multimodal polyethylene resin which has a trimodal or, most preferably, a bimodal molecular weight distribution. A bimodal polyethylene resin according to the present invention consists of one unimodal HMW ethylene interpolymer and one unimodal LMW ethylene polymer .

The HMW component characterizing the multimodal polyethylene resin of the invention comprises at least one or more, preferably one HMW ethylene interpolymer. Such ethylene interpolymer is characterized by a density in the range of from about 0.910 g/ccm, preferably of from about 0.915 g/ccm, to about 0.935 g/ccm, preferably to about 0.925 g/ccm, and a melt index of about 1.0 g/10 min or lower, preferably of about 0.05 g/10 min or lower. Advantageously, the HMW ethylene interpolymer has a melt index of about 0.02 g/10 min or higher. The HMW ethylene interpolymer contains ethylene interpolymerized with at least one alpha-olefin, preferably an aliphatic C₄–C₂₀ alpha-olefin, and/or a non-conjugated C₆–C₁₈ diolefin, such as 1,4-hexadiene or 1,7-octadiene. Although the HMW interpolymer can be a terpolymer, the preferred interpolymer is a copolymer of ethylene and an aliphatic alpha-olefin, more preferably such an alpha-olefin which has from four to ten carbon atoms. Particularly preferred aliphatic alpha-olefins are selected from the group consisting of butene, pentene, hexene, heptene and octene. Advantageously, the HMW component is present in an amount of from about 30 weight percent, preferably of from about 40 percent, to about 60 weight percent, preferably to about 50 percent (based on the total amount of polymer in the multimodal polyethylene resin). More preferably, the HMW component is present in an amount of from about 40 to about 55 percent. The molecular weight distribution as reflected by the M_w/M_n ratio of the HMW component is relatively narrow, preferably less than about 3.5, more preferably less than about 2.4.

The LMW component characterizing the multimodal polyethylene resin of the invention comprises at least one or more, preferably one LMW ethylene polymer. The LMW ethylene polymer is characterized by a density in the range of from about 0.945 g/ccm to about 0.965 g/ccm and a melt index of at least about 2.0 g/10 min or higher, preferably of at least about 5 g/10 min, more preferably of at least about 15 g/10 min or higher. Advantageously, the LMW component has a melt index of less than 2000 g/10 min, preferably of less than 200 g/10 min. A preferred LMW ethylene polymer is an ethylene interpolymer having a density in the range of from about 0.950 g/ccm to about 0.960 g/ccm

and a melt index of at least about 2 g/10 min, preferably in the range of from about 10 g/10 min to about 150 g/10 min. Preferred LMW ethylene interpolymers are ethylene/alpha-olefin copolymers, particularly such copolymers wherein the aliphatic alpha-olefin comonomer has from four to ten carbon atoms. The most preferred aliphatic alpha-olefin comonomers are selected from the group consisting of butene, pentene, hexene, heptene and octene. Advantageously, the LMW component is present in an amount of from about 40 weight percent, preferably of from about 50 percent, to about 70 weight percent, preferably to about 60 percent (based on the total amount of polymers comprised in the multimodal polyethylene resin of the invention). More preferably, the LMW component is present in an amount of from about 45 to about 60 percent.

While the alpha-olefins incorporated into a HMW component and into a LMW component comprised in a multimodal polyethylene resin of the invention may be different, preferred are such multimodal polyethylene resins, wherein the HMW and the LMW interpolymers incorporate the same type of alpha-olefin, preferably 1-butene, 1-pentene, 1-hexene, 1-heptene or 1-octene. Typically, the comonomer incorporation in the HMW ethylene interpolymers is higher than in the LMW polymer.

The multimodality of a polyethylene resin according to the present invention can be determined according to known methods. A multimodal molecular weight distribution (MWD) is reflected in a gel permeation chromatography (GPC) curve exhibiting two or more component polymers wherein the number of component polymers corresponds to the number of discernible peaks, or one component polymer may exist as a hump, shoulder or tail relative to the MWD of the other component polymer.

For example, a bimodal MWD can be deconvoluted into two components: the HMW component and the LMW component. After deconvolution, the peak width at half maxima (WAHM) and the weight average molecular weight (M_w) of each component can be obtained. Then the degree of separation ("DOS") between the two components can be calculated by the following equation:

$$DOS = \frac{M_w^H - M_w^L}{WAHM^H + WAHM^L}$$

wherein M_w^H and M_w^L are the respective weight average molecular weight of the HMW component and the LMW component; and $WAHM^H$ and $WAHM^L$ are the respective peak width at the half maxima of the deconvoluted molecular weight distribution curve for

the HMW component and the LMW component. The DOS for the bimodal resins according to the invention is at least 0.01 or higher, preferably higher than about 0.05, 0.1, 0.5, or 0.8.

WO 99/14271 also describes a suitable deconvolution technique for multicomponent polymer blend compositions.

5 Preferably, the HMW component and the LMW component are each unimodal. The MWD in the GPC curves of the individual components, e.g. the HMW component and the LMW component, respectively, does not substantially exhibit multiple component polymers (i.e. no humps, shoulders or tails exist or are substantially discernible in the GPC curve). Each molecular weight distribution is sufficiently narrow and their average molecular
10 weights are different. The ethylene interpolymers suitable for use as HMW and/or LMW component include both homogeneously branched (homogeneous) interpolymers and heterogeneously branched (heterogeneous) interpolymers.

Homogeneous ethylene interpolymers for use in the present invention encompass ethylene-based interpolymers in which any comonomer is randomly distributed within a
15 given interpolymer molecule and wherein all of the interpolymer molecules have substantially the same ethylene/comonomer ratio. Homogeneous ethylene interpolymers are generally characterized as having an essentially single melting (point) peak between -30°C and 150°C, as determined by differential scanning calorimetry (DSC). Typically, homogeneous ethylene interpolymers also have a relatively narrow molecular weight
20 distribution (MWD) as compared to corresponding heterogeneous ethylene interpolymers. Preferably, the molecular weight distribution defined as the ratio of weight average molecular weight to number average molecular weight (M_w/M_n), is less than about 3.5.

Furthermore, the homogeneity of the ethylene interpolymers is reflected in a narrow composition distribution, which can be measured and expressed using known methods and
25 parameters, such as SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Breadth Index). The SCBDI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (typically abbreviated as "TREF") as described, for example, in Wild et al, Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), in U.S. Patent
30 4,798,081 (Hazlitt et al.), or in U.S. Patent 5,089,321 (Chum et al.), the disclosures of all of which are incorporated herein by reference. CDBI is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total

molar comonomer content. The SCBDI or CDBI for the homogeneous ethylene/alpha-olefin interpolymers used in the present invention is typically higher than about 50 percent.

The homogeneous ethylene interpolymers which can be used in the present invention fall into two categories, the linear homogeneous ethylene interpolymers and the
5 substantially linear homogeneous ethylene interpolymers. Both are known in the art and commercially available.

Homogeneous linear ethylene interpolymers are interpolymers which have a homogeneous short chain branching distribution and lack measurable or detectable long chain branching. Such homogeneous linear ethylene interpolymers can be made using
10 polymerization processes which provide a uniform branching distribution, e.g., the process described by Elston in U.S. Patent No. 3,645,992, who uses soluble vanadium catalyst systems. Other single-site catalyst systems including metallocene catalyst systems, e.g., of the type disclosed in U.S. Patent No. 4,937,299 to Ewen et al., or U.S. Patent No. 5,218,071 to Tsutsui et al., are also suitable for the preparation of homogeneous linear ethylene
15 interpolymers.

The substantially linear ethylene interpolymers (SLEPs) are homogeneous interpolymers having long chain branching, meaning that the bulk ethylene interpolymers is substituted, on average, with about 0.01 long chain branches/1000 total carbons to about 3 long chain branches/1000 total carbons (wherein "total carbons" includes both backbone and
20 branch carbon atoms). Preferred polymers are substituted with about 0.01 long chain branches/1000 total carbons to about 1 long chain branches/1000 total carbons, more preferably from about 0.05 long chain branches/1000 total carbons to about 1 long chain branched/1000 total carbons, and especially from about 0.3 long chain branches/1000 total carbons to about 1 long chain branches/1000 total carbons. The presence of long chain
25 branches in such ethylene interpolymers can be determined according to methods known in the art, such as gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV).

For substantially linear ethylene polymers, the presence of long chain branching is
30 manifest from enhanced rheological properties which can be quantified and expressed, for example, in terms of gas extrusion rheometry (GER) results and/or melt flow ratio (I_{10}/I_2)

increases. The melt flow ratio of the substantially linear ethylene/alpha-olefin interpolymers can be varied essentially independently of the molecular weight distribution (M_w/M_n ratio).

The substantially linear ethylene polymers are a unique class of compounds which has been described in numerous publications, including e.g., US Patent No. 5,272,236, US Patent No. 5,278,272, and US Patent No. 5,665,800, each of which is incorporated herein by reference. Such SLEPs are available, for example, from The Dow Chemical Company as polymers made by the INSITE™ Process and Catalyst Technology, such as AFFINITY™ polyolefin plastomers (POPs).

Preferably, SLEPs are prepared using a constrained geometry catalyst. Such catalyst may be further described as comprising a metal coordination complex comprising a metal of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements and a delocalized pi (π)-bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry about the metal atom such that the angle at the metal between the centroid of the delocalized, substituted pi-bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar pi-bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted pi-bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted pi-bonded moiety. Suitable constrained geometry catalysts for manufacturing substantially linear ethylene polymers include, for example, the catalysts as disclosed in U.S. Patent No. 5,055,438; U.S. Patent No. 5,132,380; U.S. Patent No. 5,064,802; U.S. Patent No. 5,470,993; U.S. Patent No. 5,453,410; U.S. Patent No. 5,374,696; U.S. Patent No. 5,532,394; U.S. Patent No. 5,494,874; and U.S. Patent No. 5,189,192, the teachings of all of which are incorporated herein by reference.

The catalyst system further comprises a suitable activating cocatalyst.

Suitable cocatalysts for use herein include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. So-called modified methyl aluminoxane (MMAO) is also suitable for use as a cocatalyst. Aluminoxanes, including modified methyl aluminoxanes, when used in the polymerization, are preferably used such that the catalyst residue remaining in the (finished) polymer is preferably in the range of from about 0 to about 20 ppm aluminum, especially from about 0 to about 10 ppm aluminum, and more preferably from about 0 to about 5 ppm

aluminum. In order to measure the bulk polymer properties, aqueous HCl is used to extract the aluminoxane from the polymer. Preferred cocatalysts, however, are inert, noncoordinating, boron compounds such as those described in EP-A-0520732, the disclosure of which is incorporated herein by reference.

5 Substantially linear ethylene interpolymers are produced via a continuous (as opposed to a batch) controlled polymerization process using at least one reactor (e.g., as disclosed in WO 93/07187, WO 93/07188, and WO 93/07189, the disclosure of each of which is incorporated herein by reference), but can also be produced using multiple reactors (e.g., using a multiple reactor configuration as described in US Patent No. 3,914,342, the
10 disclosure of which is incorporated herein by reference) at a polymerization temperature and pressure sufficient to produce the interpolymers having the desired properties. The multiple reactors can be operated in series or in parallel, with at least one constrained geometry catalyst employed in at least one of the reactors.

 Substantially linear ethylene polymers can be prepared via continuous solution,
15 slurry, or gas phase polymerization in the presence of a constrained geometry catalyst, e.g. according to the method disclosed in EP-A-416,815, the disclosure of which is incorporated herein by reference. The polymerization can generally be performed in any reactor system known in the art including, but not limited to, a tank reactor(s), a sphere reactor(s), a recycling loop reactor(s) or combinations thereof and the like, any reactor or all reactors
20 operated partially or completely adiabatically, nonadiabatically or a combination of both and the like. Preferably, a continuous loop-reactor solution polymerization process is used to manufacture the substantially linear ethylene polymer used in the present invention.

 In general, the continuous polymerization required to manufacture substantially linear ethylene polymers may be accomplished at conditions well known in the art for
25 Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0 to 250°C and pressures from atmospheric to 1000 atmospheres (100 MPa). Suspension, solution, slurry, gas phase or other process conditions may be employed if desired.

 A support may be employed in the polymerization, but preferably the catalysts are used in a homogeneous (i.e., soluble) manner. It will, of course, be appreciated that the
30 active catalyst system forms *in situ* if the catalyst and the cocatalyst components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to

form the active catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

Heterogeneous ethylene-based polymers encompass ethylene/ α -olefin interpolymers characterized as having a linear backbone and a DSC melting curve having a distinct melting point peak greater than 115°C attributable to a high density fraction. Such heterogeneous interpolymers typically have a broader molecular weight distribution than comparable homogeneous interpolymers. Typically, heterogeneous ethylene interpolymers have a CDBI of about 50 % or less, indicating that such interpolymers are a mixture of molecules having differing comonomer contents and differing amounts of short chain branching. The heterogeneous ethylene polymers that can be used in the practice of this invention include those prepared with a coordination catalyst at high temperature and relatively low pressure. Ethylene polymers and copolymers prepared by the use of a (multi-site) coordination catalyst, such as a Ziegler-Natta catalyst or a Phillips catalyst, are generally known as linear polymers because of the substantial absence of branch chains of polymerized monomer units pendant from the backbone.

The HMW ethylene interpolymers can be a heterogeneous interpolymers or a homogeneous interpolymers, a homogeneous interpolymers being preferred. Particularly preferred HMW ethylene interpolymers are homogeneous, substantially linear HMW ethylene interpolymers. The LMW ethylene interpolymers can be a heterogeneous interpolymers or a homogeneous interpolymers, a heterogeneous interpolymers being preferred.

The multimodal polyethylene resin of the invention may be prepared by any method suitable for homogeneously blending ethylene-based polymers. For example, the HMW and the LMW component can be blended by mechanical means in the solid state, for example, in powder or granular form, followed by melting one or both, preferably both of the components, using devices and equipment known in the art. Preferably, the multimodal resin of the present invention is made by in-situ blending of the HMW component with the LMW component, e.g. using two or more reactors, operated sequentially or in parallel. According to a preferred technique, the multimodal polyethylene resin of the invention is made via the interpolymers of ethylene and the desired comonomer or comonomers, such as an aliphatic $C_4 - C_{10}$ α -olefin using a single site catalyst, e.g. a constrained geometry catalyst in at least one reactor and a multi site catalyst in at least one other reactor. The

reactors can be operated in parallel or, preferably, sequentially. Preferably, the single site catalyst, e.g. the constrained geometry catalyst is in the first reactor, and the multi site catalyst in the second reactor.

Most especially, a dual sequential polymerization system is used. In a preferred
5 embodiment of the invention, the sequential polymerization is conducted such that fresh catalyst is separately injected in each reactor. Preferably, where separate catalyst injection into each reactor is, no (or substantially no) live polymer or active catalyst is carried over from the first reactor into the second reactor as the polymerization in the second reactor is accomplished only from the injection of a fresh catalyst and monomer (and comonomer)
10 thereto.

In another preferred embodiment, the composition is manufactured using a multiple reactor system (preferably a two reactor system) in series with fresh catalyst feed injection of a soluble catalyst system into the first reactor only with process adjustments being made such that live polymer and/or catalyst species is carried over from the first reactor to a
15 subsequent reactor to effect polymerization with fresh monomer and optionally comonomer.

Most preferably, whether separate injection into each reactor is used or injection into the first reactor is used, the resulting resin is characterized as comprising component polymers having distinct, unimodal molecular weight distributions.

Most preferred is a multimodal polyethylene resin comprising a HMW interpolymer
20 designated herein as preferred, more preferred or particularly preferred and a LMW polymer designated herein as preferred, more preferred or particularly preferred, including the bimodal polyethylene resin used to exemplify the present invention.

The present invention also provides compositions comprising the multimodal polyethylene resin of the invention and at least one other additional component. Preferably,
25 such additional component is added to the multimodal polyethylene resin of the invention. Suitable additional components include, for example, other polymers, fillers or additives – with the proviso that these additional components do not adversely interfere with the desired advantageous properties of the multimodal polyethylene resin of the invention. Rather, the additional components are selected such as to support the advantageous properties of the
30 multimodal ethylene resin of the invention and/or to support or enhance its particular suitability for a desired application. Other polymers comprised in the composition of the invention means polymers which do not qualify as a HMW interpolymer or a LMW

polymer as defined herein. Advantageously, such polymers are compatible with the multimodal polyethylene resin of the invention. Preferred additional components are non-polymeric. Additives include processing aids, UV stabilizers, antioxidants, pigments or colorants. Most preferred are compositions comprising a preferred, more preferred or most preferred multimodal polyethylene resin of the invention.

The resins or compositions of the present invention can be used to manufacture a shaped article. Such article may be a single-layer or a multi-layer article, which is obtainable by suitable known conversion techniques applying heat, pressure or a combination thereof to obtain the shaped article. Suitable conversion techniques include, for example, blow-molding, co-extrusion blow-molding, injection molding, injection stretch blow molding, compression molding, extrusion, pultrusion, calendering and thermoforming. Shaped articles provided by the invention include, for example, films, sheets, fibers, profiles, moldings and pipes. Most preferred is a shaped article comprising or made from a preferred, more preferred or particularly preferred resin or composition of the present invention.

The multimodal polyethylene resins and compositions according to the present invention are particularly suitable for durable application, especially pipes - without the need for cross-linking. Pipes comprising at least one multimodal polyethylene resin as provided herein are another aspect of the present invention and include monolayer pipes as well as multilayer pipes, including multilayer composite pipes. Typically, the pipes of the invention comprise the multimodal polyethylene resin in form of a composition (formulation) which also contains a suitable combination of additives, e.g. an additive package designed for pipe applications, and/or one or more fillers. Such additives and additive packages are known in the art.

Monolayer pipes according to the present invention consist of one layer made from a composition according to the present invention comprising a multimodal polyethylene resin as provided herein and suitable additives typically used or suitable for pipe applications. Such additives include colorants and materials suitable to protect the bulk polymer from specific adverse environmental effects, e.g. oxidation during extrusion or degradation under service conditions, such as, for example, process stabilizers, antioxidants, pigments, metal de-activators, additives to improve chlorine resistance and UV protectors. Preferred multilayer composite pipes include metal plastic composite pipes and are pipes comprising

one or more, e.g., one or two, layers comprising a composition according to the present invention and a barrier layer. Such pipes include, for example, three-layer composite pipes with the general structure PE/Adhesive/Barrier or Barrier/Adhesive/ PE, or five-layer pipes with the general structure PE/Adhesive/Barrier/Adhesive/PE or

5 Polyolefin/Adhesive/Barrier/Adhesive/PE. In these structures PE stands for polyethylene layers which can be made from the same or different polyethylene compositions, preferably a PE-RT comprising composition, including at least one multimodal polyethylene composition according to the present invention. Suitable polyolefins include, for example, high density polyethylene, polypropylene and polybutylene, homopolymers and

10 interpolymers. Preferred is a multilayer composite pipe wherein at least the inner layer comprises a multimodal polyethylene resin according to the present invention in a non-crosslinked form. More preferred is a multilayer composite pipe, wherein both PE layers comprise a multimodal polyethylene resin according to the present invention. In multilayer pipes, e.g. in the three-layer and five-layer structures exemplified above, the barrier layer

15 may be an organic polymer capable of providing the desired barrier properties, such as an ethylene-vinyl alcohol copolymer (EVOH), or a metal, for example, aluminum or stainless steel.

The resins and compositions provided by the present invention are particularly suitable for use in domestic and technical pipe applications required to be operable at higher

20 temperatures, e.g. above 40°C, in particular in the range of from above 40°C to about 80°C. Such pipe applications include, for example, hot water pipes, e.g. for drinking and/or sanitary purposes and underfloor heating pipes. Such pipes may be monolayer or multilayer pipes. Preferred pipes according to the invention meet the performance requirements as defined in the norms for hot water pipes, e.g. in ISO 10508. The multimodal polyethylene

25 resin according to the present invention enables pipes combining an excellent high temperature performance, as reflected e.g. in an excellent Long Term Hydrostatic Strength at higher temperatures (well above 20°C) with good flexibility. Good flexibility facilitates e.g. pipe installation. The pipes can be produced without cross-linking, which allows improved processing economics and subsequent welding.

30 For plastic pipe applications, circumferential (hoop) stress performance as set forth in ISO 9080 and ISO 1167 is an important requirement. The long term behaviour or lifetime of plastic pipes can be predicted based on creep rupture data and curves which establish the

allowable hoop stress (circumferential stress) which a pipe can withstand without failure.

Typically, for long term predictive performance testing, candidate pipe materials are subjected to various pressures (stresses) and the lifetime at a given temperature is determined. For extrapolations to a lifetime of 50 years, e.g. at 20°C to 70°C, testing is also performed at higher temperatures. The measured lifetime curves at each temperature typically comprise a high stress, lower lifetime ductile failure mode and a lower stress, longer lifetime brittle failure mode. A schematic representation of typical lifetime curves is found at page 412, Figure 5, of the publication by J. Scheirs et al., TRIP 4 (12), 1996, pages 408 – 415. The curves can be divided into three stages, stage I representing the ductile failure stage, stage II (knee) representing a gradual change in failure mode from ductile to brittle, and stage III representing the brittle failure stage. Of particular interest are stages II and III, because these stages control the lifetime of a pipe in practice. The pipes of the present invention show an excellent hoop stress performance particularly at higher temperatures.

The invention is further illustrated by the following Examples, which, however, shall not be construed as a limitation of the invention.

Examples

Melt indices are expressed as I_2 (determined according to ASTM D-1238, condition E, 190°C/2.16 kg). The ratio of I_{10} (measured according to ASTM D-1238, Condition N, 190°C/10 kg) to I_2 is the melt flow ratio and designated as I_{10}/I_2 .

Tensile properties, such as yield stress, yield strain, maximum tensile stress and maximum elongation, stress at break and strain at break are determined in accordance with ISO 527 with test specimen 5A at a test speed of 50 mm/min.

Izod impact properties are measured according to ASTM D-256.

Flexural modulus is measured according to ASTM D-790 and average hardness D is determined according to ASTM D-2240.

The multimodal polyethylene resin used in the experiments is a bimodal ethylene interpolymer having an I_2 of 0.85 g/10 min, a density of 0.940 g/ccm and an I_{10}/I_2 of 9.8. The resin is made by in-situ blending using (continuous) solution process technology and two sequentially operated reactors. The HMW ethylene interpolymer is a homogeneous, substantially linear ethylene/octene copolymer which is made in the primary reactor using a constrained geometry catalyst. Said HMW interpolymer has an I_2 of 0.034 g/10 min and a

- density of 0.921 g/ccm. The weight average molecular weight is 228,000 and the Mw/Mn ratio is 2.1. The LMW ethylene polymer is a heterogeneous, linear ethylene/octene copolymer having an I₂ melt index of 20 g/10 min and a density of 0.953 g/ccm. The weight average molecular weight of the LMW polymer is 52,100 and the Mw/Mn ratio is 3. The
- 5 LMW ethylene polymer is made in the secondary reactor using a multi-site Ziegler-Natta (coordination) catalyst. The ratio of HMW copolymer to LMW copolymer in the bimodal polyethylene resin is 40 to 60.

The resin has the following tensile, impact and other properties (each given value represents the average of five measurements):

10	Yield stress [MPa]:	21
	Yield strain [%]:	13
	Maximum tensile stress [MPa]	36
	Maximum elongation [%]	760
	Stress at break [MPa]	36
15	Strain at break [%]	760
	Flexural modulus [MPa]	955
	Hardness D	61
	Izod at 20°C [J/m]	238
	Izod at - 40°C [J/m]	8

Monolithic pipes made from the above resin are subjected to hydrostatic pressure testing using the test method described in ISO 1167 (1996) and water as the internal and external test medium. The pipes have nominal dimensions of 16 mm x 2 mm.

5 The hoop stress results are given in Table 1.

Temperature [°C]	Hoop Stress [MPa]	Failure time [h]*	Failure Mode*
20	10.57	> 3096	
20	10.54	> 10344	
20	10.44	> 10344	
20	10.40	> 4056	
20	10.32	> 4056	
80	5.65	656	ductile
80	5.59	1245	ductile
80	5.52	> 5952	
80	5.49	> 3600	
80	5.45	> 3600	
80	5.42	> 5952	
80	5.35	> 4056	
80	5.34	> 3600	
80	5.30	> 5952	
80	5.25	> 3600	
110	2.91	> 3912	
110	2.89	> 3912	
110	2.84	> 2616	
110	2.79	> 3912	
110	2.47	> 11976	
110	2.11	> 11976	

* “>” indicates that the specimen is still under test without failure. In such cases, no failure mode can be indicated.

10 The pipes made from the bimodal polyethylene resin show an excellent hoop stress performance, especially at high(er) temperatures. Surprisingly, no knee (stage II) reflecting a change in failure mode from ductile to brittle is manifest, yet. Test results already go beyond the control points for PE-RT according to DIN 16883 (1.9 MPa/8760 h at 110°C) and PEX according to ISO 10146 (2.5 MPa/8760 h at 110°C).

WHAT IS CLAIMED IS:

1. A polyethylene resin having a multimodal molecular weight distribution, said resin being further characterized in that it has
- 5 (a) a density in the range of from about 0.925 g/ccm to about 0.950 g/ccm, and
- (b) a melt index (I_2) in the range of from about 0.05 g/10 min to about 5 g/10 min,
- and
- (c) comprises at least one high molecular weight (HMW) ethylene interpolymer and at least a low molecular weight (LMW) ethylene polymer, wherein
- 10 (d) the HMW component comprises at least one or more ethylene interpolymers having a density in the range of from about 0.910 g/ccm to about 0.935 g/ccm, and a melt index of about 1.0 g/10 min or lower, and
- (e) the LMW component comprises at least one or more ethylene polymers having a density in the range of from about 0.945 g/ccm to about 0.965 g/ccm and a melt
- 15 index of at least about 2.0 g/10 min or higher.
2. The polyethylene resin according to claim 1 which has a bimodal molecular weight distribution and consists of one unimodal HMW ethylene interpolymer and one unimodal LMW ethylene polymer.
- 20
3. The polyethylene resin according to any of claims 1 to 2, wherein the LMW ethylene polymer is an ethylene interpolymer and has a density of 0.960 g/ccm or lower.
- 25
4. The polyethylene resin according to any of claims 1 to 3, wherein the HMW and/or the LMW ethylene interpolymer is a homogeneous, substantially linear interpolymer.
5. A composition comprising the multimodal polyethylene resin according to
- 30 any of claims 1 to 4 and at least one other additional component.

6. The composition according to claim 5 wherein the at least one other additional component is selected from the group consisting of fillers and additives.

5 7. A shaped article comprising the multimodal polyethylene resin according to any of claims 1 to 5.

8. The shaped article according to claim 7 which is a pipe.

10 9. The pipe according to claim 8 which is operable at temperatures of above 40°C.

10. The pipe according to claim 8 which is a hot water pipe, preferably such pipe meeting the performance requirements defined in the ISO 10508 standard.

15

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/27503

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	page 3, line 33 -page 4, line 1; example 7 ---	8-10
X	EP 0 778 289 A (MOBIL OIL CORP) 11 June 1997 (1997-06-11)	1-7
Y	page 3, line 29 -page 3, line 54; example 7 ---	8-10
Y	WO 01 02480 A (DAMM ELKE ;ELENAC GMBH (DE); BOEHM LUDWIG (DE); SCHULTE ULRICH (DE) 11 January 2001 (2001-01-11) cited in the application the whole document ---	8-10
A	US 5 539 076 A (NOWLIN THOMAS E ET AL) 23 July 1996 (1996-07-23) the whole document -----	1

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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